Nonequilibrium generalization of the Nernst's heat theorem

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Nonequilibrium: Physics, Stochastics and Dynamical Systems
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Motivating example

Myosin molecular motor [R. Dean Astumian, Biophysical Journal (2010) 2401]

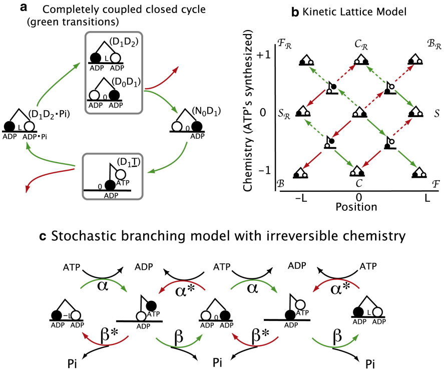

Figure: Chemical cycle for Myosin V stepping

Collaboration

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General issues

- Many open thermodynamic systems can be modeled as stochastic (even Markovian) processes
- Lack of general "statistical" theory for far-from-equilibrium processes
- Even the structure of nonequilibrium steady states is to a large extent unexplored
- Details of dynamics seem to play an essential role
- Need for exact symmetries and simplifying asymptotic schemes
- Link between equilibrium thermodynamic description and nonequilibrium transport properties still not clear

Praha

Stochastic models

Markovian dynamics – Master equation

$$\frac{\partial \rho_t(x)}{\partial t} + \sum_y j_t(x,y) = 0, \qquad j_t(x,y) = \rho_t(x)\lambda(x,y) - \rho_t(y)\lambda(y,x)$$

- constitutive relation between time-dependent occupation probabilities and local currents
- dynamics encoded in transition rates $\lambda(x,y)$
- states x may represent either single-body or many-body discrete states of system
- linear algebraic problem

$$\frac{\partial \hat{\rho}_t}{\partial t} = \hat{W}\hat{\rho}_t$$

Thermodynamic versus kinetic aspects

Local detailed balance principle

- *Asymmetry* of transition rates $\leftrightarrow$ *Dissipation* along transition channel

$$\lambda(y \to x) = \lambda(x \to y)\, e^{-\Delta S_{env}(x \to y)}$$

- *symmetric* factors (= local time-scales) depend on *kinetic details*
  - Kramers theory etc. but no general guiding principle!

Equilibrium systems – global detailed balance

$$\log \frac{\lambda(x,y)}{\lambda(y,x)} = \Delta S_{\text{env}} = \beta\, Q(x,y) = \beta\,[E(x) - E(y)]$$

Nonequilibrium – nonpotential structure of dissipation functions

$$Q(x,y) = E(x) - E(y) + W(x,y), \quad \text{or} \quad \beta(\text{x,y}) \neq \beta$$

Thermodynamic versus kinetic aspects

Questions to be discussed

1. What is the role of kinetics in stationary properties of the system?
2. How to describe the NESS in general?
3. How to find low-temperature patterns analogous to ground states in equilibrium and what would be corresponding phase diagrams?
4. How to compute relevant currents in such a low-temperature asymptotics, e.g., for the ratchets?
5. How to go beyond stationarity, in particular, how to see quasistatic responses to changes of thermodynamic parameters (e.g., the steady heat capacity)?

Heat bounds, ordering and Blowtorch theorem

Questions:

1. How much the kinetic details actually matter out of equilibrium?
2. What can we say about stationary occupations from the heat function $Q(x, y)$ alone?

Result: From Boltzmann weights to general heat bounds

$$\exp\left[-\beta \max_{D: x\to y} Q(D)\right] \leq \frac{\rho(x)}{\rho(y)} \leq \exp\left[-\beta \min_{D: x\to y} Q(D)\right]$$

- If $Q(D) \geq 0$ along all non-intersecting paths $D : x \to y$ then $\rho(x) \leq \rho(y)$ independently of kinetic details
  - partial ordering of states in terms of the heat function alone
  - strictly positive dissipation for all $D : x \to y$ yields separation of occupations exponentially in β

Heat bounds, ordering and blowtorch theorem

We can prove it from the algebraic Matrix-tree theorem which yields the tree-graph representation of stationary distributions

$$\rho(x) = \frac{1}{Z} \underbrace{\sum_{T} \prod_{(y,y') \in T_x} \lambda(y, y')}_{w(T_x)} \qquad T_x - \text{oriented spanning in-tree to } x$$

with the local detailed balance

$$\frac{w(T_x)}{w(T_y)} = e^{-\beta Q(D_{x\to y})}$$

- To exploit it more we next look into the low-temperature asymptotics

Heat bounds, ordering and blowtorch theorem

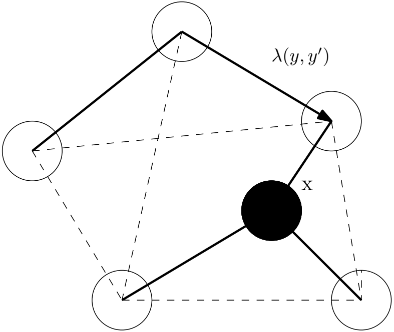


Figure:

NESS representation of dynamics

Three complementary ingredients for complete description of NESS:

1. stationary occupation probabilities $\rho(x)$
2. local currents $j(x,y) = \rho(x)\lambda(x,y) - \rho(y)\lambda(y,x)$
3. dynamical activity landscape $\gamma(x,y) = \rho(x)\lambda(x,y) + \rho(y)\lambda(y,x)$

Note: Attempts to construct nonequilibrium ensembles without considering the dynamical activity are wrong in general!

Main issues

Question 1:

What are dominant states and currents, and where to look for dominant dynamical activity in low-temperatures?

Question 2:

What is the low-temperature asymptotics of thermodynamic process? Is there a generalized Nernst theorem for the excess heat?

Low-temperature asymptotics

Zero-temperature limit of continuous (diffusion) dynamics is a deterministic process

$$\frac{dx_t}{dt} = F(x_t) + \frac{1}{\sqrt{\beta}}\text{"(Gaussian-)noise"}$$

- Freidlin-Wentzell large deviation theory

Discrete stochastic dynamics ill-defined in the limit $\beta \longrightarrow +\infty$!

We can still apply the algebraic representation of NESS!

Low-temperature asymptotics

Modified Arrhenius representation of transition rates

$$\lambda(x,y) = \frac{p(x,y)}{\tau(x)} = a(x,y;\beta)\, e^{-\beta[\Gamma(x)+U(x,y)]}$$

in terms of

1. log-asymptotic escape rate $-\Gamma(x) = \lim_{\beta\to\infty} \frac{1}{\beta} \log \sum_y \lambda(x,y)$
   - life-time is asymptotically $\tau(x) \asymp e^{\beta\Gamma(x)}$
2. log-asymptotic transition probabilities $U(x,y) = \Gamma(x) - \lim_{\beta\to\infty} \frac{1}{\beta} \log \lambda(x,y)$
   - transition probabilities are asymptotically $p(x,y) \asymp e^{-\beta U(x,y)}$
   - $U(x,y) \geq 0$ and $U(x,y) = 0$ defines preferred transitions
     - represented by oriented graph of preferred transitions
3. sub-exponential factor $a(x,y) = e^{o(\beta)}$

Low-temperature asymptotics

Asymptotic form of stationary distribution

$$\rho(x) = \frac{1}{Z} A(x)\, e^{\beta[\Gamma(x)-\Theta(x)]}\left(1 + O(e^{-\beta\epsilon})\right), \qquad \epsilon > 0$$

Up to a correction negligible at low temperatures, it is given in terms of:

1. (log-asymptotic) life-time of states $\Gamma(x)$
2. accessibility function

$$\Theta(x) = \min_T U(T_x)\,, \qquad U(T_x) = \sum_{(y,y')\in T_x} U(y,y') \geq 0$$

3. sub-exponential factor

$$A(x) = \sum_{T\in M(x)} \prod_{(y,y')\in T_x} a(y,y') = e^{o(\beta)}$$

where the sum is only over those trees minimizing $U(T_x)$

The accessibility function Θ

Recall: The accessibility function measures the minimal "penalization" along trees rooted at state x:

$$\Theta(x) = \min_T U(T_x)\,, \qquad U(T_x) = \sum_{(y,y')\in T_x} U(y,y') \geq 0$$

Components,their ordering and attractors

- If there is a path $D : x \rightsquigarrow y$ consisting of preferred transitions only, $U(D){=}0$, then

$$\Theta(x) \geq \Theta(y)$$

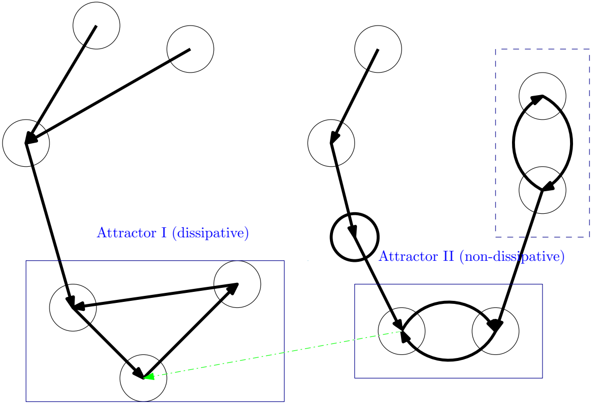
- natural decomposition of state space Ω into disjoint subsets $\Omega_1, \Omega_2, \ldots$ so that
  - each Ω_i is a (maximal) strong component of the graph of preferred transitions = within Ω_i all states are mutually freely accessible
  - $\Theta-$function is constant within each component Ω_i
  - the components can be partially ordered according to their value Θ_i

$$\Omega_i \rightsquigarrow \Omega_j \quad \Rightarrow \quad \Theta_i \geq \Theta_j$$

  - the terminal components, i.e. those minimizing $\Theta-$function, are attractors

The accessibility function Θ

Figure:



The accessibility function Θ

Result: Algorithm to compute the function Θ

$$\Theta(x) = \min(U(T_x) \,|\, \text{all trees T connecting state x with all attractors})$$

Corollary: Partial order on states and properties of attractors

1. $U(x,y) = 0 \implies \Theta(x) \geq \Theta(y)$
2. $x,\ y \in$ Attractor $\implies \Theta(x) = \Theta(y)$
3. $U(x,y) = 0$ such that $x \notin$ Attractor, $y \in$ Attractor $\implies \Theta(x) > \Theta(y)$
4. A -unique attractor $\implies \Theta(\text{A})=0$

Dynamical interpretation of Θ—function

Local dynamical activity

$$\Upsilon(x) = \sum_y \rho(x)\lambda(x,y)$$

The overall dynamical activity counts the total number of transitions per unit time

$$\sum_x \Upsilon(x) = \frac{1}{2}\sum_{x,y}[\rho(x)\lambda(x,y) + \rho(y)\lambda(y,x)]$$

Low-temperature asymptotics of dynamical activity

$$\Upsilon(x) \asymp \rho(x)\lambda(x,y)|_{U(x,x*)=0} \asymp \frac{1}{Z}\, e^{-\beta\Theta(x)}$$

- Θ—function provides the exponential asymptotics of local dynamical activity
- dominant contribution to (global) dynamical activity comes from an attractor

Dominant states

Dominant states are solutions to the variational problem

$$\Gamma(x) - \Theta(x) = \max$$

- Unique dominant state $\Rightarrow \rho(x^*) = 1 - O(e^{-\beta\epsilon})$
  - analogous to non-degenerate ground state in equilibrium
- In degenerate case the sub-expontial factor $A(x)$ is needed to distinguish the "true" mostly populated states
- Possible frustration between (long / short) life-time and (bad / good) accessibility
- Dominant states may lie outside dynamical attractors
  - patological thermodynamic properties

Absolutely dominant states

A remarkable simplification arises when there exists an *absolutely* dominant state x^* such that

1. it is maximally accessible, $\Theta(x^*) = 0$;
2. it has the maximal life-time among all states, $\Gamma(x^*) = \max_y \Gamma(y)$.

Properties of systems with A. D. states

- all dominant states are *absolutely* dominant
- probability of excitations has the asymptotics

$$\rho(x) \asymp e^{-\beta\left[\Gamma(x^*)-\Gamma(x)+\Theta(x)\right]}, \quad \Theta(x) = \min_{D:\, x^* \to x} U(D)$$

  - the minimizers correspond to typical excitation paths for x

Excursion: Path low-temperature asymptotics

$P^\Delta(D = x_0 x_1 \ldots x_n)$ = probability that starting from x_0, the system passes the sequence of states $x_0 \to x_1 \to \ldots \to x_n$ within time $e^{\beta\Delta}$.

Result 1: excitation /technical assumptions skipped/

Asymptotically for $\Delta = \Gamma(x^*) - \epsilon$,

$$P^\Delta(D = x^* x_1 \ldots x_n) \asymp \exp[-\beta I^\Delta(D)]$$

with the rate function

$$I^\Delta(D) = \Gamma(x^*) - \Gamma(x_n) + U(D)$$

- By comparing with the above representation,

$$\rho(x) \asymp \max_{D:\, x^* \rightsquigarrow x} P^\Delta(D)\,, \qquad \Delta = \Gamma(x^*) - \epsilon$$

Excursion: Path large-deviation problem

$P^\Delta(D = x_0 x_1 \dots x_n)$ = probability that starting from x_0, the system passes the sequence of states $x_0 \to x_1 \to \dots \to x_n$ within time $e^{\beta\Delta}$.

Result 2: relaxation /technical assumptions skipped/

Asymptotically for $\Delta = \Gamma(x^*) - \epsilon$,

$$P^\Delta(D = x\, x_1 \dots x^*) \asymp \exp[-\beta I^\Delta(D)]$$

with the rate function

$$I^\Delta(D) = U(D)$$

Hence $\max_{D:\, x \rightsquigarrow x^*} P^\Delta(D) \asymp 1$ and the maximum is attained for the paths made of preferred transitions

- the excitation and relaxation paths may not be the reversal of each other!

Heat bounds revisited

Heat function is given as

$$Q(x,y) = \Gamma(y) - \Gamma(x) + U(y,x) - U(x,y)$$

For every state x we have

- excitation paths D_x^+ from x^* to x that minimize $U(D)$

$$-Q(D_x^+) \leq \Gamma(x^*) - \Gamma(x) + U(D_x^+)$$

- relaxation paths D_x^- from x to x^* for which $U(D_x^-) = 0$

$$Q(D_x^-) = \Gamma(x^*) - \Gamma(x) + U([D_x^-]^\dagger)$$

Heat bounds revisited

Corollary: Improved heat bounds for systems with A. D. states

$$-Q(D_x^+) \leq -\lim_{\beta\to\infty} \frac{1}{\beta} \log \rho(x) \leq Q(D_x^-)$$

- if $D_x^- = [D_x^+]^\dagger$ then $Q(D_x^-) = -Q(D_x^+)$ and we obtain the equality!
- immediate consequences for the heat function:
  - $Q(D_x^-) \geq 0$ – second law for spontaneous relaxation
  - $Q(D_x^+) + Q(D_x^-) \geq 0$ – second law for typical excitation-relaxation cycles
- An asymptotic equality in terms of heat and penalization function:

$$\rho(x) \asymp e^{-\beta[\,Q(D_x^-)+U(D_x^+)-U([D_x^-]^\dagger)\,]}$$

Current asymptotics

- The low-temperature asymptotics of local currents may not be specified by the attractors and asymptotic occupations only, due to mutual cancellation of dominant terms

$$j(x,y) = \rho(x)\lambda(x,y) - \rho(y)\lambda(y,x)$$

- A finer representation of local currents is needed
- Current is naturally associated with positively dissipative circuits = closed non-intersecting paths such that

$$Q(C) = \sum_{(z,z')\in C} Q(z,z') > 0$$

Low-temperature asymptotics of circuit currents

$$j(C) \asymp e^{-\beta\Theta(C)}, \qquad \Theta(C) = \min_{T_C} U(T_C)$$

with the minimum over all in-trees to the (positively dissipative) circuit C

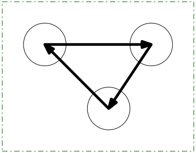
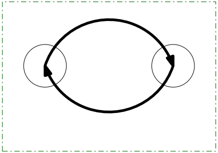
Dissipative versus non-dissipative attractors

Dissipative attractors – contain a circuit C such that $Q(C) > 0$

$$\frac{J(C)}{\Upsilon} \asymp 1$$

Non-dissipative attractors – only trivial circuits

$$\frac{J(C)}{\Upsilon} \asymp e^{-\beta\epsilon}, \qquad \epsilon > 0$$

Figure:  

Model: Driven lattice gas on the ring

Configurations are $x = (x_1, \ldots, x_L)$ with $x_k = 0$ (empty) or 1 (occupied).

Dynamics is Kawasaki (= particle exchange) with transition rates

$$\lambda(x \to x^{(k,k+1)}) = \exp\Big(\frac{\beta}{2}\big[H(x) - H(x^{(k,k+1)}) + E(x_k - x_{k+1})\big]\Big)$$

and the Hamiltonian

$$H(x) = -J\sum_i x_i x_{i+1} + K\sum_i x_{i-1}x_{i+1}, \qquad J > 0$$

- particle number $N = \sum_i x_i$ is a conserved quantity
- dynamics is translation-invariant

Phase diagram for dynamical activity (N=3)

- sharp transitions only in the zero temperature limit
- "non-structural" (red-line) versus "structural" (blue-line) transitions
- discontinuous transition along the line $E = J$, $K > 2J$ with the current as an order parameter

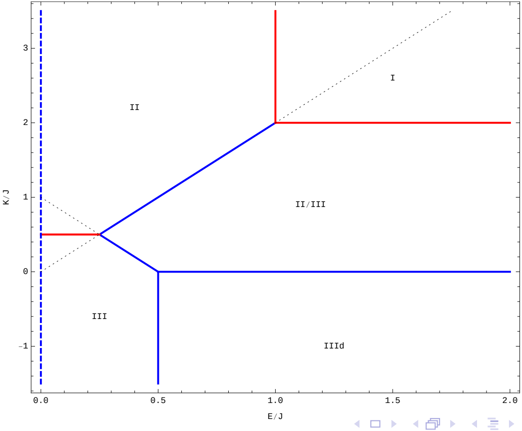


Figure:

List of attractors (N=3)

- I dissipative attractor with all particles detached and moving along the ring
- II non-dissipative symmetry-breaking attractor with 2-particle cluster and a single particle separated but attached to the cluster
- III non-dissipative symmetry-breaking attractor with 3-particle cluster
- IIId dissipative attractor with 3-particle cluster as a whole traveling along the ring
- II/III dissipative attractor with 3-particle cluster moving along the ring via separation of a single particle

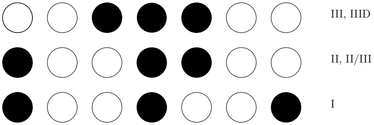


Figure:

Steady-state thermodynamics

The total heat released along a quasistatic process passing a sequence of steady states parametrized by α_t, $0 \le t \le \tau$ has the representation

$$\langle Q\rangle = \underbrace{\int_0^\tau \langle q(x_t;\alpha_t)\rangle^{\alpha_t}\,dt}_{steady-state\ heat\ O(\tau)} + \underbrace{\int_{\alpha_0}^{\alpha_\tau} \langle \nabla_\alpha V(x;\alpha)\rangle^{\alpha}\cdot d\alpha}_{geometric\ (\text{“Berry”})\ heat} + \underbrace{O(\tau^{-1})}_{non-quasistatic}$$

- Steady-state heat is the integral stationary flux

$$\langle q(x;\alpha)\rangle^\alpha = \frac{1}{2}\sum_{x,y} Q^\alpha(x,y)\, j^\alpha(x,y) \ge 0$$

- geometric contribution derives from the dissipation function (or “quasipotential”) counting heat along relaxation to stationarity

$$V(x;\alpha) = \frac{1}{2}\sum_{y,y'}\int_0^\infty Q^\alpha(y,y')\,[\underbrace{j_t^\alpha(y,y')}_{relaxation\ from\ x} - j^\alpha(y,y')]$$

  - non-equilibrium generalization of the energy function

Steady-state thermodynamics

The total heat released along a quasistatic process passing a sequence of steady states parameterized by α_t, $0 \leq t \leq \tau$ has the representation

$$\langle Q \rangle = \underbrace{\int_0^\tau \langle q(x_t;\alpha_t)\rangle^{\alpha_t}\, dt}_{steady-state\ heat\ O(\tau)} + \underbrace{\int_{\alpha_0}^{\alpha_\tau} \langle \nabla_\alpha V(x;\alpha)\rangle^\alpha \cdot d\alpha}_{geometric\ (\text{"Berry"})\ heat} + \underbrace{O(\tau^{-1})}_{non-quasistatic}$$

Warm-up: *equilibrium* process

- $\langle q(x;\alpha)\rangle^\alpha = 0 \rightarrow$ no divergences in quasistatic limit
- $V(x;\alpha) = E_\alpha(x) - \langle E_\alpha\rangle^\alpha$ and the geometric contribution to the heat is given by the Clausius equality

$$\int_{\alpha_0}^{\alpha_\tau} \langle \nabla_\alpha V(x;\alpha)\rangle^\alpha \cdot d\alpha = -\int_{\alpha_0}^{\alpha_\tau} \beta^{-1} dS(\alpha)$$

  with (Shannon) entropy

$$S(\alpha) = -\sum_x \rho^\alpha(x) \log \rho^\alpha(x)$$

- Remains true close to equilibrium (up to leading order in nonequilibrium driving)

Steady-state thermodynamics

The total heat released along a quasistatic process passing a sequence of steady states parameterized by α_t, $0 \leq t \leq \tau$ has the representation

$$\langle Q \rangle = \underbrace{\int_0^\tau \langle q(x_t;\alpha_t)\rangle^{\alpha_t}\, dt}_{steady-state\ heat\ O(\tau)} + \underbrace{\int_{\alpha_0}^{\alpha_\tau} \langle \nabla_\alpha V(x;\alpha)\rangle^{\alpha} \cdot d\alpha}_{geometric\ (\text{``Berry''})\ heat} + \underbrace{O(\tau^{-1})}_{non-quasistatic}$$

Non-degenarate system with unique A. D. state

- The dissipation function is asymptotically the heat released along optimal relaxation path

$$V(x;\alpha) = Q_x^{\alpha,-} + O(e^{-\beta\epsilon}), \qquad V(x^*;\alpha) = O(e^{-\beta\epsilon})$$

  - finite positive zero-temperature limit
    $\rightarrow$ well-defined effective energy of states!

Steady-state heat capacity

The total heat released along a quasistatic process passing a sequence of steady states parameterized by α_t, $0 \leq t \leq \tau$ has the representation

$$\langle Q \rangle = \underbrace{\int_0^\tau \langle q(x_t;\alpha_t)\rangle^{\alpha_t}\, dt}_{steady-state\ heat\ O(\tau)} + \underbrace{\int_{\alpha_0}^{\alpha_\tau} \langle \nabla_\alpha V(x;\alpha)\rangle^{\alpha} \cdot d\alpha}_{geometric\ (\text{``Berry''})\ heat} + \underbrace{O(\tau^{-1})}_{non-quasistatic}$$

For slow temperature changes, the geometric heat can be expressed in terms of generalized heat capacity

$$C_\alpha = -\left\langle \frac{\partial V}{\partial T} \right\rangle^\alpha = \sum_x \left\langle V(x;\alpha)\, \frac{d \log \rho(x;\alpha)}{dT} \right\rangle^\alpha, \qquad T = \frac{1}{\beta}$$

- for equilibrium systems it reduces to the equilibrium heat capacity $C = T\frac{\partial S}{\partial T}$
- far from equilibrium it can take negative values

Steady-state heat capacity (unique A. D. state)

Combing with the stationary distribution

$$\rho(x) \asymp e^{-\beta\Psi(x)}, \qquad \Psi(x) = \Gamma(x^*) - \Gamma(x) + U(\text{typical excitation path to x})$$

the steady-heat capacity is asymptotically

$$C = -\beta^2 \left\langle V \frac{\partial \log \rho}{\partial \beta} \right\rangle^\alpha = \beta^2 \rho(x_1) V(x_1) \Psi(x_1) + \text{"exp. damped corrections"}$$

- $x_1 -$ the lowest (= the most probable) excitation
- C>0 and it is bounded from above and below by the heat capacity of the equilibrium systems with "generalized energies" V and Ψ, respectively

Generalized Nernst law for systems with A. D. states

Steady heat capacity is *positive* and goes *exponentially to zero* in the zero-temperature limit.

- but in general not true for non-absolutely dominant states

References

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